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POLYMERIZATION OF OILS BY A HIGH-FREQUENCY DISCHARGE WITHOUT ELECTRODES

Prof G. M. Panchenkov
I. P. Vlasov

/The procedure described here offers a convenient method of increasing the viscosity and density of an oil, while at the same time lowering its congelation point. The method presumably can be applied to the conversion of otherwise useless petroleum fractions into lubricating oils of acceptable quality. Tables and figures are appended./

In the course of one of the preceding investigations (1), research was done on the polymerization of aviation oil and the oil fraction of cracking residue through the action of a high-frequency discharge without electrodes at an electromagnetic field frequency of 33 Mc. The variations of the following were studied: density of oils, average molecular weight, viscosity, surface tension on the air-oil and oil-water bounderies, percentage content of aromatic and unsaturated hydrocarbons, and congelation temperature. Variations of the values of the above constants, after the action of a high-frequency discharge without electrodes, were studied in a vacuum where extraneous gases were absent and for different durations of the discharge.

Experimental Part

As a source of high-frequency electromagnetic oscillations, a vacuum tube generator was used; it was set up according to Holborn's scheme, with 800 watts power, and was described in one of our works (2). For the study of the action

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of these discharges upon oil, 150 cc of mineral oil were poured into a glass ampule /closed vessel/, which was placed between the plates of a condenser hooked up in a circuit that was connected inductively with the circuit of the ultrashort-wave generator. The ampule was set horizontally and subjected to a uniform rotary motion by an electric motor. To avoid excessive cracking of the contents, the ampule was cooled with circulating water. The surface of the ampule, moreover, did not become heated. To create a vaccuum in the ampule, air and dissolved gases liberated by the oil were evacuated with the aid of a two-stage oil pump until the dissolved gases were fully expelled.

After the elimination of the gas, the ampule was subjected to rotary motion and the generator of electromagnetic oscillations turned on. Over the whole surface of the oil a gaseous electric discharge was set off, and throughout the whole gaseous space there extended a bright blue glow. After specific periods of time, the ampule was opened and the oil subjected to examination. Aviation oil and the oil fraction of the cracking residue (boiling at 170-350°) were chosen as subjects of the investigation. The density of the oils was determined by a pycnometer. The results of the determinations of density (d_4^{20}) are cited in Table 1.

As is evident from this table, the density of the oils increases after the action of the discharge upon them, and this increase is the greater the longer the duration of the discharge.

Viscosity of the oils was determined with Ostwald's viscometer. The results of the measurements of comparative viscosity are cited in Table 2.

The increase in viscosity after the same duration of the action of the discharge is greater for aviation oil than for the oil fraction of the cracking residue, i.e., the greater the average molecular weight of the oil, the greater the increase in viscosity. Moreover, the viscosity grows with the increase of the duration of the action of the discharge. Figures 1 and 2 show the variation of the viscosity of oils with the variation of the duration of the action of the discharge (isothermic viscosity).

The results of the calculation of temperature dependence of the viscosity of oils for the temperature of 35° C are cited in Table 3 /sic/.

The molecular weights of the oils were determined by the cryoscopic method. Benzene was used as the solvent. The results of the determinations of molecular weights are cited in Table 4.

The molecular weight of oils increases with the increase of the duration of the action of the charge /see Figures 1 and 2/.

The surface tensions of oils on the air-oil and oil-water boundaries were measured by the maximum bubble pressure method. The results of the measurements are cited in Table 5.

As is evident from the data cited, the surface tension of oils on the air-oil boundary remains constant after the action of the high-frequency discharge without electrodes, while on the oil-water boundary it increases significantly; and, in the latter case the greater the increase in surface tension, the greater the duration of the action of the discharge.

For the initial oils, as for oils subjected to the action of the discharge, determinations were made of the percentage content of aromatic hydrocarbons (by the aniline point method) and the percentage content of unsaturated hydrocarbons (by McIlwain's simplified method of bromination) (3). The results of the analysis are cited in Table 6.

The percentage content of aromatic hydrocarbons in aviation oil remains practically constant, while in the oil fraction of the cracking residue it increases. The increase in percentage content of aromatic hydrocarbons takes place, in all probability, on account of dehydrogenation of naphthenic hydrocarbons (1). The percentage content of unsaturated hydrocarbons (containing double bonds) in aviation oil rises with the increase of the duration of the discharge, while in oil of the cracking residue it remains practically constant.

The congelation temperature of oils which have been subjected to the action of the discharge is lowered, and this lowering effect is greater the longer the action of the discharge. The congelation temperature was determined by the standard method. The results are cited in Table 7.

Examination of the experimental results obtained verifies the possible elementary processes, discussed earlier, which originate as a result of the action of a discharge.

Conclusions

1. Investigation was made of the action of a high-frequency discharge without electrodes on aviation oil and the oil fraction of the cracking residue in a vacuum at an electromagnetic field frequency of 33 Mc for varying durations of the action of the discharge.

2. It was found that the increase in viscosity and molecular weight of oils was greater, the longer the duration of the action of the discharge.

3. The surface tension of oils on the air-oil boundary remains unchanged after the action of the charge, but on the oil-water boundary it increases with the increase of the duration of the discharge.

4. The percentage content of aromatic hydrocarbons in the case of aviation oil remains constant, while in the case of the oil fraction of the cracking remnant it rises with the increased duration of the action of the discharge.

5. The congelation temperature of oils subjected to the action of the discharge was lower than that of the initial oils, and the lowering effect was greater the longer the oil was subjected to the action of a discharge.

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3. Chemical Composition of Petroleum Crudes and Petroleum Products (Khimicheskiy sostav neftey i neftyanykh produktov), ONTI, 1935, p 381.

[Appended tables and figures follow.]

Table 1. Density

T in °C	Aviation Oil				Oil Fraction of Cracking Residue			
		After Action of a Discharge During				After Action of a Discharge During		
	Initial	10 hr	20 hr	30 hr	Initial	10 hr	20 hr	30 hr
20	0.8920	0.8928	0.8937	0.8946	0.9843	0.9850	0.9860	0.9864
30	0.8864	0.9802*	0.8916	0.8921	0.9782	0.9787	0.9800	0.9828
40	0.8802	0.8823	0.8828	0.8844	0.9714	0.9724	0.9734	0.9738
50	0.8744	0.8760	0.8813	0.8820	0.9650	0.9660	0.9665	0.9672
60	0.8688	0.8711	0.8718	0.8768	0.9572	0.9577	0.9586	0.9591
80	0.8666	0.8668	0.8675	0.8681	0.9426	0.9438	0.9445	0.9459

[*sic]

Table 2. Viscosity [relative]

T in °C	Aviation Oil				Oil Fraction of Cracking Residue			
		After Action of a Discharge During				After Action of a Discharge During		
	Initial	10 hr	20 hr	30 hr	Initial	10 hr	20 hr	30 hr
20	456.0	809.8	823.6	848.9	40.81	43.78	52.16	53.62
30	226.1	417.1	427.3	428.5	23.03	31.53	33.54	35.84
40	125.1	249.8	251.9	255.5	18.53	20.19	20.96	28.42
50	72.9	159.0	161.5	165.6	13.64	14.40	14.17	15.13
60	53.86	100.4	101.7	103.2	9.15	9.89	10.39	8.83
80	33.46	46.58	46.55	47.2	5.68	6.01	6.13	6.26

Table 3

Duration of Action of Discharge (in hr)	Aviation Oil	Oil Fraction of Cracking Residue
0	0.11201	0.0664
10	0.1002	0.0635
20	0.1002	0.0755
30	0.1026	0.0708

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Table 4. Molecular Weight

Duration of Action of Discharge (in hr)	Aviation Oil	Oil Fraction of Cracking Residue
0	636.8	246.3
10	654.7	254.7
20	680.3	265.1
30	691.5	282.9

Table 5. Surface Tension

Surface Tension in Ergs/Sq Cm

Duration of Action of Discharge (in hr)	Aviation Oil		Oil Fraction of Cracking Residue	
	Air/Oil	Oil/Water	Air/Oil	Oil/Water
0	36.94	52.14	34.39	34.30
10	36.94	61.74	34.39	37.42
20	36.94	63.60	34.39	40.54
30	36.94	74.09	34.39	45.21

Table 6. Percentage Content of Aromatic Hydrocarbons and Unsaturated Hydrocarbons

Duration of Action of Discharge (in hr)	Aviation Oil		Oil Fraction of Cracking Residue	
	Aromatic Hydrocarbons (%)	Unsaturated Hydrocarbons (%)	Aromatic Hydrocarbons (%)	Unsaturated Hydrocarbons (%)
0	6.93	11.82	14.0	33.3
10	6.65	11.87	16.1	32.2
20	6.93	13.27	17.6	32.8
30	5.82	13.85	18.0	33.4

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Table 7. Congelation Temperature

Duration of Action of Discharge (in hr)	Congelation Temperature in ° C: Aviation Oil	Congelation Temperature in ° C: Oil Fraction of Cracking Residue
0	-26	-43
10	-27.5	-43.6
20	-30	-44
30	-32	-44.8

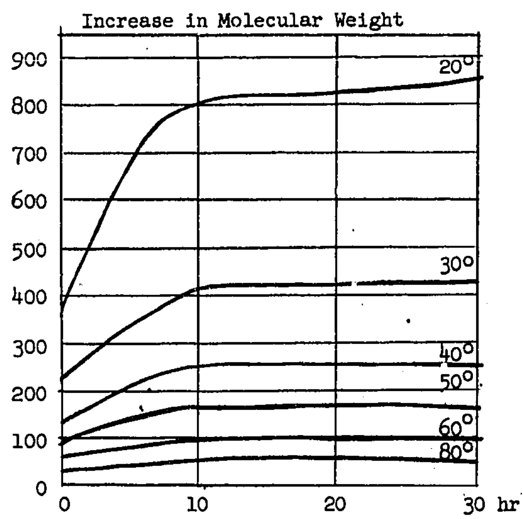

Figure 1. Aviation Oil

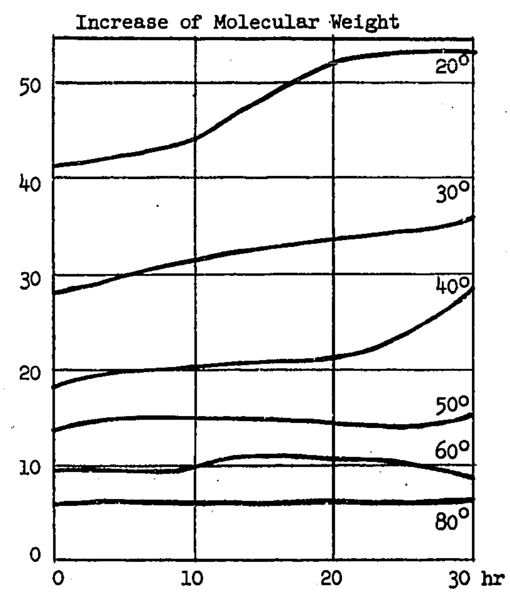

Figure 2. Oil Fraction of Cracking Residue

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